

# PATENT SPECIFICATION

(11) 1388 733

1388 733

- (21) Application No. 28740/72 (22) Filed 20 June 1972  
 (31) Convention Application No. 155127 (32) Filed 21 June 1971 in  
 (33) United States of America (US)  
 (44) Complete Specification published 26 March 1975  
 (51) INT CL<sup>2</sup> C23C 7/00  
 (52) Index at acceptance  
 C7F 1G1 2H 2Z3 3E 4G  
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## (54) METHOD OF APPLYING A POROUS LAYER TO A METAL SUBSTRATE

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to a method of applying a porous layer to a surface of a metal substrate. More significantly, the present invention relates to a method of applying a porous boiling surface layer to a substrate as for example, to the surface of a metal sheet, and more particularly, to the exterior surface of a metal tube.

It is known that the effectiveness of heat exchange apparatus for boiling liquids is greatly increased by the provision of a porous surface layer characterized by the presence of a multitude of small pores bonded on a thermally conducting wall of heat exchange apparatus for transferring heat to a liquid to be boiled.

In the prior art processes, the porous layer has been produced by sintering small particles of a heat conductive metal, such as copper, to the wall supplying heat to the boiling liquid. It is known to sinter 1 to 50 micron-size particles to produce a porous layer having a thickness of about 0.1 to 1.0 mm. It is also known to modify the sintering operation by providing the particles with an extremely thin coating of a temporary binder. Thereafter, the binder is air dried and subsequently completely eliminated during the sintering operation.

Porosity of the surface layer as produced by this sintering operation may be controlled to some extent by selection of metal particle size, but complete control of porosity cannot be attained because the particles must be tightly packed so that each particle contacts adjacent particles to enable the sintering

operation to produce molecular bonding between these particles.

According to the present invention there is provided a method of applying a porous layer to a surface of a metal substrate, which method comprises mixing particles of a primary material which is metallic with particles of a secondary material to provide a uniform mixture of the two types of particles, applying the mixture by flame deposition to a surface of the substrate to form thereon a molecularly bonded but inhomogeneous layer of the primary material containing regions of pure secondary material not alloyed with nor interdiffused with the primary material, and thereafter eliminating the secondary material from regions of pure secondary material to provide a porous continuously-bonded layer of metallic primary material bonded to the metal substrate.

The metal substrate may be in the form of a sheet, or preferably, in the form of a tube. If desired the surface of the metal substrate to be provided with a porous layer may be initially roughened to provide a better key. As in the prior art the thickness of the porous layer may be from 0.1 to 1 mm.

Preferably the secondary material is also a metal and particles of secondary material are eliminated from the layer formed by flame deposition by leaching.

The invention is illustrated by the accompanying drawings in which:

Figure 1 is a photomicrograph of a flame sprayed coating of copper and zinc before leaching,

Figure 2 is a view similar to Figure 1 after leaching with dilute hydrochloric acid, and

Figure 3 is a graph comparing the operation of a tube having a porous layer applied by a method in accordance with this invention with an otherwise identical plain tube.

The drawings are described in more detail below.

In the method of the present invention the primary material particles are deposited to form a layer on a surface of a metal substrate

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by flame spraying, and are bonded without appreciable interdiffusion, or alloying, except to bond particles of the primary material, with particles of the secondary material uniformly distributed throughout the layer. Thus, depending upon the percentage of primary and secondary materials provided in particle form, increased porosity may be obtained by dissolution of the secondary material different from the primary metal particles intended to make up the porous layer.

The ultimate porosity and the physical characteristics of the porous layer produced in accordance with the present invention thus depends upon particle size and also upon the proportions of the two different materials used. The porous layer also has improved physical characteristics because the deposition by flame spraying provides for molecular bonding as the layer is built up in thickness. This produces results which are superior to sintering as will now appear.

In sintering, solid metal particles are brought together so that continuous particle-to-particle contact is established. To form a porous structure a mass of particles is subjected to heat without substantial pressure and the individual particles become molecularly bonded together essentially by a process of interdiffusion of metal atoms. Thus, if the particles are substantially homogeneous mixture of metals, the molecular bonding between adjacent particles is constituted by an amorphous bridge and within each of the particles there is a zone of alloyed metal in which the proportions vary.

In this prior art method in order to obtain the molecular interdiffusion, it is necessary to maintain the mass of particles at elevated temperature for a protracted period. The diffusion continues while the particles are at elevated temperature and if maintained at elevated temperature for a sufficient period, where are particle are of two different metals, eventually the particles become a uniform, homogeneous alloy.

On the contrary, where flame spraying technique is employed, the particles are heated to accurately controlled temperatures and the temperature at which they are brought into contact with the surface of deposit may also be accurately controlled. The control, as is well understood, is accomplished by controlling the temperature of the flame and the dimensions of the flame. The particles traverse the flame and the temperature of the particles thus is controlled by the temperature of the flame and the length of the flame. The heated particles are projected from the flame on to the surface of a metal substrate. The particles may also be permitted to traverse a controlled distance of air before contacting the surface, during which time they cool to some extent. Thus

the particles, although deposited by flame spraying, may be substantially cool and congealed as they contact the surface of the metal substrate.

By maintaining the flame at a low temperature and short, so that the particles traverse only a relatively short distance of flame, particles of materials, even those of relatively low melting point, may be projected by flame spraying at substantially any desired temperature, including temperatures at which the particles are not substantially melted.

The essential difference between sintering and flame spraying is the accurate control of physical structure which may be effected by flame spraying, as contrasted with sintering, to produce a porous material.

While reference has been made to the use of particles of two different metals, it is also possible to produce a deposit of a single metal mixed with particles of a non-metallic material such as a plastics material, in which the particles of the plastics material limit the points of contact between adjacent particles of metal and provide voids when the plastics material is eliminated, for example, by leaching out with a suitable solvent. If plastics material is used, at least 5% by volume is needed.

In accordance with a specific example of the present invention, producing the materials as illustrated in the Figures of the accompanying drawings, two powder constituents were simultaneously sprayed onto the substrate. The substrate was a grit-blasted unalloyed copper tube. The particles as applied by flame spraying comprised a mixture of 10% by weight of zinc metal powder (secondary material) with a maximum diameter of 44 microns (-325 ASTM mesh) with 90% by weight of copper metal powder (primary material) in which 50% of the copper metal powder was 53 to 74 microns in diameter (-200+270 ASTM mesh), and the remaining 50% was 74 to 110 microns in diameter (-140+200 ASTM mesh). In general, particle size may range from 25 to 150 microns. This mixture was sprayed through an oxygen-acetylene torch onto the copper tube. The spraying was conducted at a relatively low flame temperature to minimize alloying of the copper and zinc metal constituents.

The conditions under which the mixture of zinc and copper particles are deposited by flame spraying are such that while the copper particles, the primary material, are heated to an elevated temperature, they are not melted in whole or in part. The zinc particles, the secondary material, have a lower melting point, and are completely melted and are deposited along with the solid copper particles. At this time part of the zinc forms an alloy bond of copper-zinc alloy between adjacent particles of copper. A substantial portion of the zinc congeals in the form of separate particles

which may in most cases be molecularly bonded to adjacent copper particles by alloy bonds, again of copper-zinc alloy.

5 After spraying, the tube surface was immersed in 10% hydrochloric acid at room temperature for about three hours to remove the unalloyed zinc, the secondary material, from the layer.

10 The leaching operation does not dissolve the copper-zinc alloy bonds between adjacent copper particles so that the copper particles remain bonded together. However, wherever there is a separate congealed particle of zinc, it is dissolved by the hydrochloric acid and leached out of the metallic layer, thus leaving a void therein. Where a particle of zinc is connected by alloy bonds with copper particles at opposite sides thereof, it appears that the zinc particle is dissolved and leached out of the layer, although the alloy phase is not leached out.

The tube was then washed, dried and subjected to heat transfer evaluation tests.

25 The heat transfer characteristics of a tube having a porous layer applied by the method of the present invention were compared to those of a plain copper tube. Water was circulated inside a copper tube immersed in liquid freon (registered Trade Mark). This test simulates chilled water cooling systems where-  
30 in warm water is cooled by boiling liquid freon, the cooled water is circulated to an air conditioning unit and the water from the air conditioning unit, now warmer, is returned to the copper tube immersed in boiling freon.

40 The ordinate of Figure 3 represents heat flux (transmission), units of heat per hour per unit of area. The abscissa represents differential temperature between boiling freon and water. It can be seen from Figure 3 that the tube having a porous layer applied by the method of the present invention transfers as much heat as a plain tube and yet only  
45 requires about 1/10 as much differential temperature driving force. Thus, to transfer the same amount of heat across a plain tube of the prior art, almost ten times as much temperature differential is required when compared to that required with the tube having  
50 a porous layer applied by the method of the present invention. Those skilled in the art will realize the significant savings in utilities and equipment cost which can be realized with  
55 the tube of the present invention.

60 In general terms, the proportions of the metal particles which are to form the residual porous matrix (primary material) should be between 80 and 95% by weight and the secondary material, which is to be removed by dissolution, shall accordingly be from 5 to 20% by weight.

65 It should be noted that the primary material may be an alloy or a physical mixture of two or more metals. Fairly pure copper particles

are preferred because of their excellent heat transfer characteristics and also because of their resistance to the hydrochloric acid leaching step, but it is conceivable that mixtures of copper with other metals or other metals or alloys may be used. All that is required is that the primary metal particles forming the residual porous matrix be able to withstand subsequent elimination of the secondary material, for example, in a leaching step.

70 It will be observed by comparing Figures 1 and 2 that in Figure 1 the porous matrix formed by the molecularly bonded particles of copper and zinc is quite porous but is nevertheless substantially less porous than the same material after removal of the zinc constituents, or secondary materials, by leaching. It will be apparent, of course, that particularly in Figure 2, the small discrete light areas are not in fact unbonded particles but  
80 merely represent filamentary portions of the copper matrix. In fact, all of the copper metal deposited in the layer by the method of the present invention is inter-bonded so that a continuously bonded highly porous surface layer is produced. This illustrated layer is characterized by the substantially complete absence of closed cells. Thus, liquid can penetrate by capillary action or otherwise into  
85 any open space within the bonding layer and may escape therefrom as vapor.

Moreover, the porosity resulting from flame deposition and leaching is such that individual pores within the porous layer are interconnected so that liquid may flow from one pore to an adjacent pore as liquid within the adjacent pore is vaporized and expelled therefrom.

100 The porosity of the layer applied by the method of the invention may be altered by varying the proportions of the constituent materials, the only limitation being that the metal particles which are to form the residual matrix or boiling layer must be in sufficient proportion to provide a continuously bonded, although extremely porous, layer.

105 As previously noted, the method of depositing the particles by flame spraying has the advantage of permitting control of porosity and the attainment of a higher degree of porosity than is practically possible with sintering. It is preferred to control deposition of the layer, together with the other factors which effect porosity as mentioned above, so as to obtain a porosity of between 40 and 70% by volume. Porosity indicates the percentage of the void volume, as contrasted to the total volume.

110 The present invention may be employed to provide a porous surface layer on the exterior of plain tubing, e.g., unalloyed copper tube, or it may be applied to corrugated tube through which the heating medium is circulated to transfer heat to the liquid to be boiled at the exterior surface of the tube.

115 In the foregoing, reference has specially 130

been made to the application of a mixture of primary and secondary metal particles, but the invention may be used to apply a mixture of primary metal particles with a plastics secondary material which may subsequently be removed by an organic solvent. For this purpose fluorocarbons such for example as polytetrafluoroethylene may be used as the plastics secondary material.

#### 10 WHAT WE CLAIM IS:—

1. A method of applying a porous layer to a surface of a metal substrate, which method comprises mixing particles of a primary material which is metallic with particles of a secondary material to provide a uniform mixture of the two types of particles, applying the mixture by flame deposition to a surface of the substrate to form thereon a molecularly bonded but inhomogeneous layer of the primary material containing regions of pure secondary material not alloyed with nor interdiffused with the primary material, and thereafter eliminating the secondary material from regions of pure secondary material to provide a porous continuously-bonded layer of metallic primary material bonded to the metal substrate.

2. A method as claimed in claim 1, wherein the surface of the metal substrate to be provided with a porous layer is initially roughened.

3. A method as claimed in claim 1 or claim 2, wherein the metal substrate is in the form of a sheet.

4. A method as claimed in claim 1 or claim 2, wherein the metal substrate is in the form of a tube.

5. A method as claimed in claim 4, wherein the porous layer is applied to the exterior surface of the tube.

6. A method as claimed in any one of the preceding claims, wherein particles of primary material have a size of from 25 to 150 microns.

7. A method as claimed in any one of the preceding claims, wherein the thickness of the porous layer is from 0.1 to 1 mm.

8. A method as claimed in any one of the

preceding claims, wherein the mixture of primary and secondary materials comprises from 80 to 95% by weight of primary material and from 5 to 20% by weight of secondary material.

9. A method as claimed in any one of the preceding claims, wherein the secondary material is also a metal and particles of secondary material are eliminated from the layer formed by flame deposition by leaching.

10. A method as claimed in claim 9, wherein the secondary material is zinc and the leaching is carried out with dilute hydrochloric acid.

11. A method as claimed in any one of the preceding claims, wherein the primary material is copper.

12. A method as claimed in claim 11 when dependent on claim 10, wherein the zinc particles have a maximum diameter of 44 microns and 50% of the copper particles have a diameter of 53 to 75 microns and the remaining 50% have a diameter of 74 to 110 microns.

13. A method as claimed in any one of the preceding claims, wherein the secondary material is chosen such that the pores within the layer are in communication with each other.

14. A method as claimed in any one of the preceding claims, wherein the particle sizes and the relative proportions of the primary and secondary materials and the flame deposition conditions are chosen to provide a layer having a porosity of from 40 to 70% by volume.

15. A method of applying a porous layer to a surface of a metal substrate as claimed in claim 1 and substantially as hereinbefore described.

16. A metal substrate having a porous layer applied to a surface thereof by a method as claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

FIG. 1

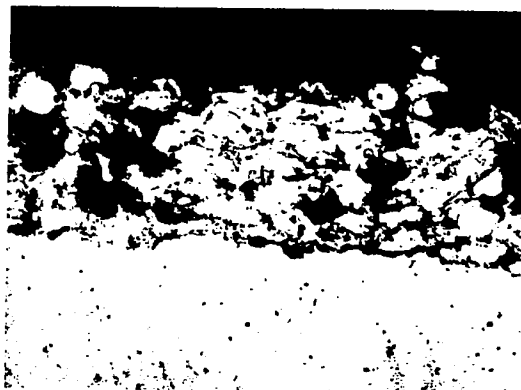


FIG. 2



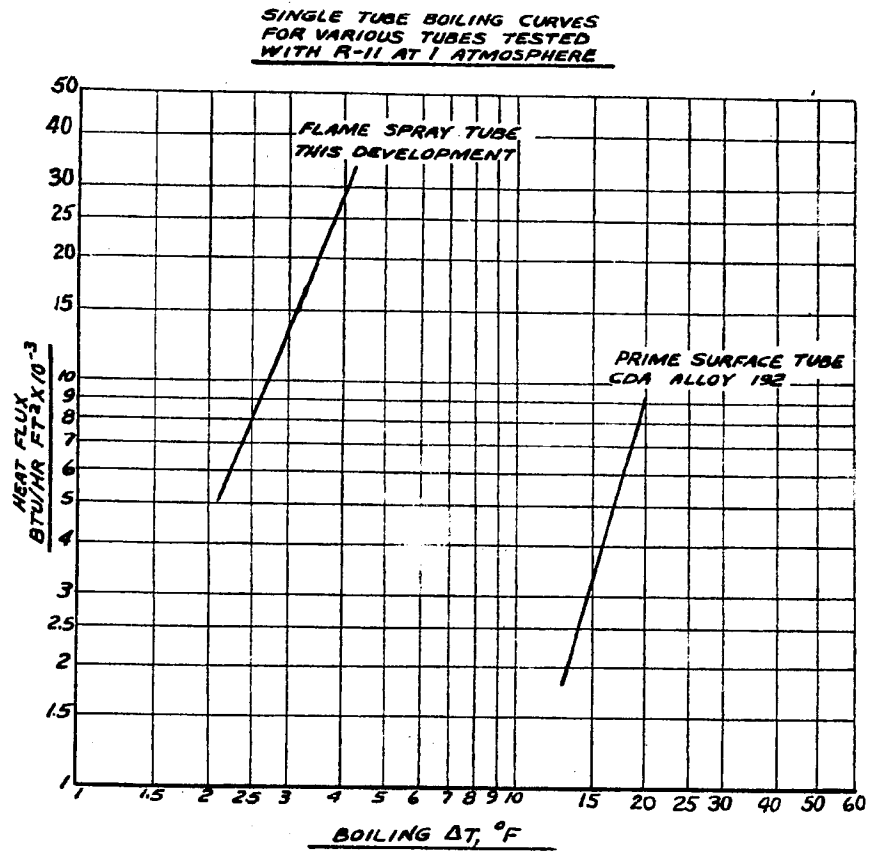


FIG.3